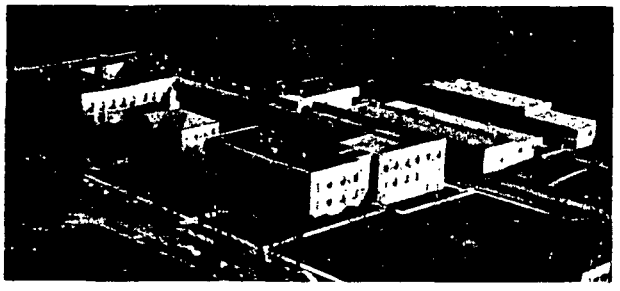

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RESEARCH ON SMELT-WATER REACTIONS

Report Four

to

Advisory Technical Committee

1. Fourth Activity Report of Project Co-ordinator, IPC Project 2419.
2. Progress Report of The Babcock & Wilcox Company to November 6, 1964.
3. Progress Report of Combustion Engineering, Inc. to November 6, 1964.

November 30, 1964

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

FOURTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

November 19, 1964

This research project is being conducted for the Board of Directors created by a group of manufacturers of chemically produced wood pulp, pursuant to Sponsorship Agreements (this group of companies hereinafter referred to as the Smelt-Water Research Group). This report, or any portions thereof, may not be quoted, reproduced, or disseminated outside the member companies of the Smelt-Water Research Group without the express written approval of the Advisory Technical Committee, The Babcock & Wilcox Company, Combustion Engineering, Inc., and The Institute of Paper Chemistry.

In view of the tentative nature of research results and the early stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

Distribution:

Board of Directors
Advisory Technical Committee
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The Babcock & Wilcox Company - Messrs. Darmstadt, Markant (3), Moran
Combustion Engineering, Inc. - Messrs. Hochmuth, Lawler, Nelson (2), Ulmer
The Institute of Paper Chemistry - Messrs. Smith, Strange, Whitney

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

FOURTH ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

This report covers activities of the Project Co-ordinator from August 28 to November 15, 1964. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in attached reports, covering the period from August 15 through November 6. The Project Co-ordinator is in frequent contact with the laboratory research, and visited the B&W Research Center on October 2 and CE's Kreisinger Development Laboratory on October 8.

Work on the chemical aspects of smelt-water explosions is proceeding at the B&W Research Center. The several avenues of investigation are expected to develop relevant information, but the work is presently at an intermediate stage. A good beginning has been made, experimental apparatus and techniques are being developed and several indications have resulted from the work to this point.

The decomposition of black liquor, by heating, has been shown by B&W to be a heat-absorbing process at all stages. Since no heat is generated, black liquor decomposition, of itself, cannot be a primary factor in furnace explosions. However, the decomposition of black liquor has also been shown to evolve, at relatively low temperatures, significant quantities of gaseous products. These gases are believed to be combustible, and can be a hazard when a hearth is "blacked out" with black liquor. The studies relating to black liquor decomposition, when completed, will have an important bearing on considerations of emergency shutdown procedures.

The investigation of physical aspects of smelt-water explosions, being conducted by Combustion Engineering, continues to enlarge our understanding of this complex problem. The technique that has been developed to produce small explosions safely on a laboratory scale is a promising research tool. The attached report contains a number of important indications. The experiments involving explosions, when water was added continuously above the surface of the smelt, have shown the possibility that explosions can also be produced as a result of surface interaction of smelt and water. In this case, the physical mixing of the two materials is not the result of strong agitation such as occurs when one material is forcibly injected or poured rapidly into another. Recognition of this possibility broadens our concepts of the ways in which furnace explosions may be caused.

The CE experiments on the effect of additions of other materials to water or, in earlier work, to smelt are particularly significant. Assuming that physical smelt-water explosions are caused by the heating of water to a high pressure within an encapsulating shell of solidified smelt, then the ability to prevent the formation of a strong shell may be a promising approach to preventing explosions. Dr. J. A. Van den Akker, Chairman of the Mathematics and Physics Section of The Institute of Paper Chemistry, first called to our attention the possibility that such encapsulating shells might have unusually high strength, since their surfaces, in contact with internal water or external molten smelt, would be expected to be free from surface cracks or defects. Such imperfections, if they were present, would provide points for local stress concentrations. This phenomenon, known as the Joffe effect, is further discussed in the CE report and may be an important factor in our considerations.

The reader's attention is particularly directed to Section D, Effect of Smelt-Weakening Additives in the attached CE report. Earlier CE and B&W

research has shown that pure sodium carbonate does not produce smelt-water explosions. However, in the present program, CE has reported* that 15 and 20% additions of sodium chloride to sodium carbonate produced violent smelt-water explosions. The effect of sodium sulfide additions in increasing the explosive violence of sodium carbonate-sodium sulfide smelts has been amply demonstrated, and the CE report referred to above has also shown that additions of sodium sulfide to sodium carbonate greatly increase the physical strength of solidified smelt. This evidence of the relationship between smelt-water explosions and the strength of the encapsulating shell of solidified smelt emphasizes the importance of the work being done at CE to further explore this behavior.

As the research on smelt-water reactions proceeds, we have maintained liaison with others interested in the problem. On October 5 and 6, the Project Co-ordinator attended meetings in the Boston area of the Black Liquor Recovery Boiler Advisory Committee and its subcommittee on Emergency Shutdown Procedures. Contact with these activities continues to add to our understanding of the practical problems of recovery furnace safety.

In the effort to arrive as rapidly as possible at a satisfactory understanding of the smelt-water reactions, the Project Co-ordinator has discussed with a number of organizations and individuals their possible contribution of information or participation in various phases of the project. In this respect, talks have been held with representatives of the following:

Explosion Research Laboratory, U. S. Bureau of Mines

Combustion and Explosives Research, Inc.

Stanford Research Institute

Illinois Institute of Technology Research Foundation

*Combustion Engineering, Inc., May 15 to August 15, 1964 Progress Report, p. 9.

Arthur D. Little, Inc.

Illinois Institute of Technology

Massachusetts Institute of Technology

One area that seems particularly critical to the project is the need for a more penetrating and conclusive observation of the results of actual recovery furnace explosions. If we can definitely determine the explosion mechanism, and this has not clearly resulted from past observations, a program for remedial action can then be undertaken. To gain better insight into the explosion mechanism, it is believed that we can benefit from the assistance of consultants who are experts in damage analysis and the interpretation of explosive phenomena. A second area where expert consultation may also be effective is in developing an accelerated experimental program on the relation between the composition and mechanical strength of solidified smelt, hopefully to lead to the development of an acceptable nonexplosive smelt formulation. The Project Co-ordinator is preparing recommendations to the Advisory Technical Committee, for subsequent consideration by the Board of Directors, for appropriate action toward engaging consulting assistance from qualified experts.

THE INSTITUTE OF PAPER CHEMISTRY

Howard S. Gardner

Howard S. Gardner
Project Co-ordinator, Project 2419
Senior Research Associate
Administrative Staff

PROGRESS REPORT

FOR THE PERIOD OF AUGUST 15, 1964 TO NOVEMBER 6, 1964

TO

H. S. GARDNER, PROJECT COORDINATOR,
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

December 1, 1964

PROGRESS REPORT OF THE BABCOCK & WILCOX COMPANY
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between August 15 and November 6, 1964 and the present status of this project. As outlined in previous reports, our objective is to determine which chemical reactions take place between the smelt-char-combustion gas system and water that result in explosive reactions. Once these have been determined, the variables affecting the formation of explosive combinations will be investigated so that a basis can be established for recommending preventive measures and shut-down procedures. A further objective is to determine the thermal decomposition products and characteristics of black liquor in order to formulate better emergency shut-down procedures.

STATUS

Background Studies

A visit was made to the Pulp and Paper Research Institute of Canada in order to discuss topics of interest to this project with J. J. O. Gravel. Gravel has shown that the thermal decomposition of black liquor yields significant quantities of combustible (and explosive) gases. These discussions confirmed that additional studies of black liquor decomposition were required. This is discussed later in this report.

As a further effort to understand the processes taking place in an operating Kraft recovery boiler, and so that an operating theoretical model can be better examined, our plans have included field studies of an operating unit. Preliminary testing has further substantiated the views and experience of other investigators that such studies are extremely difficult. A high level of effort is required in this area. As a result, this phase was de-emphasized during this period

in order to get our experimental laboratory program under way. Further studies are, however, being planned for the next period.

Chemical Equilibrium Studies

In addition to gaining an insight to the formation of explosive constituents from smelt/char and water, the theoretical reaction products, both gaseous and condensed, are of interest from the point of view of understanding the chemistry of a Kraft recovery unit.

The computer approach to the required complex equilibrium calculations has been extended to the calculation of relatively simple gaseous-condensed phase systems treating each condensed species as a separate phase. Initially, the method was checked out by adding arbitrary, known amounts of carbon and sodium carbonate to a previously converged, all gaseous system and the proper recovery, by computer, was obtained.

As it is our objective to compute the equilibrium for black liquor combustion under conditions of 30-110% total air over a range of temperatures from 800°K - 1600°K (981°F - 2431°F), an initial composition representing 30% total air was fed to the computer to test the program for the 26 component system under consideration. Results were obtained at 800°K, 900°K and 1000°K (981°F, 1161°F and 1341°F), but at higher temperatures convergence of the results was slow and an undue amount of computer time was required. Convergence criteria are being relaxed and preliminary results to date show a marked reduction in the time required.

In order to illustrate this approach, Tables I and II show the results obtained to date for the case of 30% total air. Table I is the complete printout of all the species considered and the results are in exponential form. In order to make the tabulation more readily usable the results are also printed

out in Table II for the major species found, in volume percent (gas phase) and lbs/100 lbs of feed (condensed phase) in non-exponential form.

No further hand calculations have been carried out on the reactions of water with smelt-char constituents. It is anticipated that if a further refinement of the computer program can be made, e.g. by treatment of the molten smelt as an ideal solution, calculations will be made on this system taking all of the possible reactions into account.

Experimental Studies On Smelt-Water Reactions

It is the purpose of our experimental studies to determine through experiment what chemical reactions take place between smelt and water. It is our plan to investigate initially the reactions of single smelt components with water vapor. Furthermore, test data can best be interpreted if the reaction between a solid phase with a gas phase (water vapor) is first studied. Our initial experiments are therefore being carried out with solid sodium sulfide and water vapor.

The apparatus described in the last report has been built; in addition, a stainless steel protective shield was fabricated for installation around the reaction vessel. The apparatus was tested initially using a charge of sodium carbonate as the reactant. The melting point of sodium carbonate was used as a check on the temperature measurement. During this run it was noted that the stainless steel cover oxidized and that the silicon carbide showed some attack. The cover was flame sprayed with alumina and a graphite liner inserted in the crucible.

One preliminary test at 1400°F has been carried out using sodium sulfide as the solid phase reactant and in helium containing water vapor at a partial pressure of 4.5 mm. The reaction vessel operates at ≈8 PSIG. In spite of this there was significant in-leakage of air. This air could have reacted with any hydrogen

and/or hydrogen sulfide produced. This may account for the fact that neither hydrogen or H_2S was detected as reaction products. Another feature of this test was the inability to make a material balance of the amount of water input and output. It therefore appears that solid Na_2S is capable of holding water at this temperature, possibly as a hydrate. The significance of this finding is not yet apparent.

Further experiments with sodium sulfide are being carried out in a tubular furnace arrangement similar to that described by Rosen. Such an arrangement is better adapted to the study of solid-gas reactions and can be carried out more quickly. The crucible type apparatus will be used for liquid melts and some refinements are necessary to prevent air in-leakage.

It was noted in the last report that a satisfactory method for preparing anhydrous sodium sulfide has been developed. As this preparation is somewhat time-consuming, we have attempted to purchase this material. Although a large number of potential suppliers have been contacted, only one has agreed to furnish this chemical. As this one has not as yet delivered the Na_2S it appears that he is having difficulty meeting this commitment. As a result, progress has not been as fast as expected.

Black Liquor Decomposition Studies

A better understanding of some of the characteristics of the thermal decomposition of black liquor is desirable from several viewpoints. In the first place, it could furnish a better understanding of the mechanisms which lead to the burning and subsequent smelt formation. In addition, it would be desirable to know what takes place when the bed is quenched by spraying black liquor during an emergency shut-down.

Experiments were carried out on a black liquor of 53.9% solids using both thermogravimetric analysis (TGA) and differential thermal analysis (DTA)

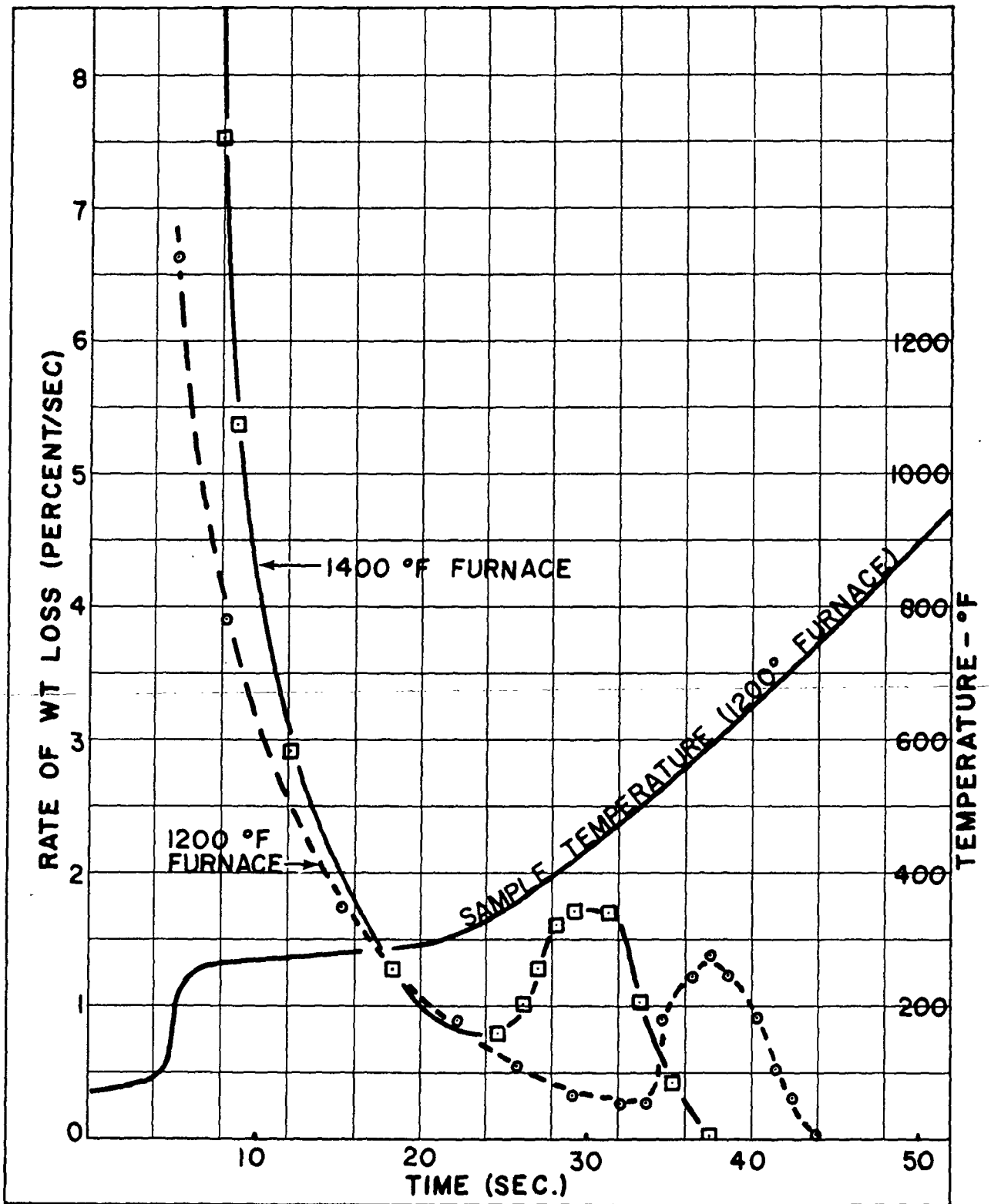
techniques. In the TGA work a known weight of sample was quickly inserted in the TGA furnace, under a helium atmosphere and, by means of a recording balance, the weight change was observed as a function of time. The experiments were carried out at furnace temperatures of 1200°F and 1400°F; higher temperatures caused such rapid weight losses that they could not be determined accurately even with a high-speed recorder. A thermocouple in the sample gave a rough indication of the sample temperature. Figure 1 shows the results of the analysis of the data obtained and is a differential plot showing the rate of decomposition with time. This plot shows that, as might be expected, the bulk of the water is eliminated rapidly and that during this time the temperature remains relatively low. After the moisture is eliminated, the thermal decomposition of the black liquor solids in the 1200° furnace takes place between about 500 and 700°F, resulting in the formation of gaseous decomposition products. Such gaseous products, for the liquor investigated, amounted to approximately 14% by weight of the total sample, or 26% of the total solids.

Differential thermal analysis of this sample was carried out primarily to determine whether there was any heat liberated during decomposition in an inert atmosphere. The sample was placed in the DTA apparatus, in a helium atmosphere, programmed for a heating rate of 27°F/min and heated to 1795°F. Only endothermic reactions were observed; a major endotherm at 230°F, corresponding to the release of water, and minor endotherms at 895°, 1275° and 1435°F.

The implications of this work are that, first of all, the decomposition of black liquor is a completely endothermic reaction, hence this factor by itself is not a factor in the observed explosions. On the other hand, the decomposition of black liquor, after the moisture is eliminated, results in a large volume of gas at relatively low temperatures. Although no analysis of gas was made, it seems certain that such gas is highly explosive and this should be considered

TEMPERATURE	800 K (981 F)	900 K (1161 F)	1000 K (1341 F)
SPECIES(GASEOUS)	VOLUME PERCENT		
CO	0.380E 01	0.141E 02	0.282E 02
CO2	0.145E 02	0.113E 02	0.460E 01
H2	0.111E 02	0.162E 02	0.187E 02
H2O	0.100E 02	0.562E 01	0.212E 01
CH4	0.174E 01	0.843E 00	0.343E 00
N2	0.567E 02	0.513E 02	0.460E 02
O2	0.339E-35	0.240E-25	0.244E-21
H2S	0.196E 01	0.569E 00	0.179E-01
NH3	0.853E-02	0.454E-02	0.270E-02
SO2	0.967E-11	0.625E-12	0.833E-10
SO3	0.125E-32	0.320E-22	0.128E-21
SO	0.881E-11	0.130E-12	0.228E-10
NO	0.199E-16	0.734E-18	0.228E-17
NO2	0.262E-41	0.570E-33	0.684E-29
COS	0.232E-01	0.167E-01	0.890E-03
CS2	0.373E-14	0.563E-05	0.395E-07
S2	0.234E-13	0.600E-06	0.487E-08
NA2	0.253E-20	0.209E-15	0.380E-11
NA	0.160E-09	0.895E-07	0.225E-04
C2N2	0.546E-16	0.147E-17	0.635E-17
SPECIES(CONDENSED)	LBS / 100 LBS OF FEED		
C(S)	0.798E 01	0.538E 01	0.158E 01
NA2CO3(C)	0.178E 02	0.138E 02	0.120E 02
NA2S(C)	0.000E-99	0.294E 01	0.431E 01
NA2SO4(C)	0.000E-99	0.000E-99	0.000E-99
NA2O(C)	0.000E-99	0.000E-99	0.000E-99
NAOH(C)	0.000E-99	0.000E-99	0.000E-99
TOTAL	0.258E 02	0.222E 02	0.179E 02

TABLE I. EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR (30% TOTAL AIR).



SUBJECT DIFFERENTIAL TGA PLOT OF BLACK LIQUOR DECOMPOSITION	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
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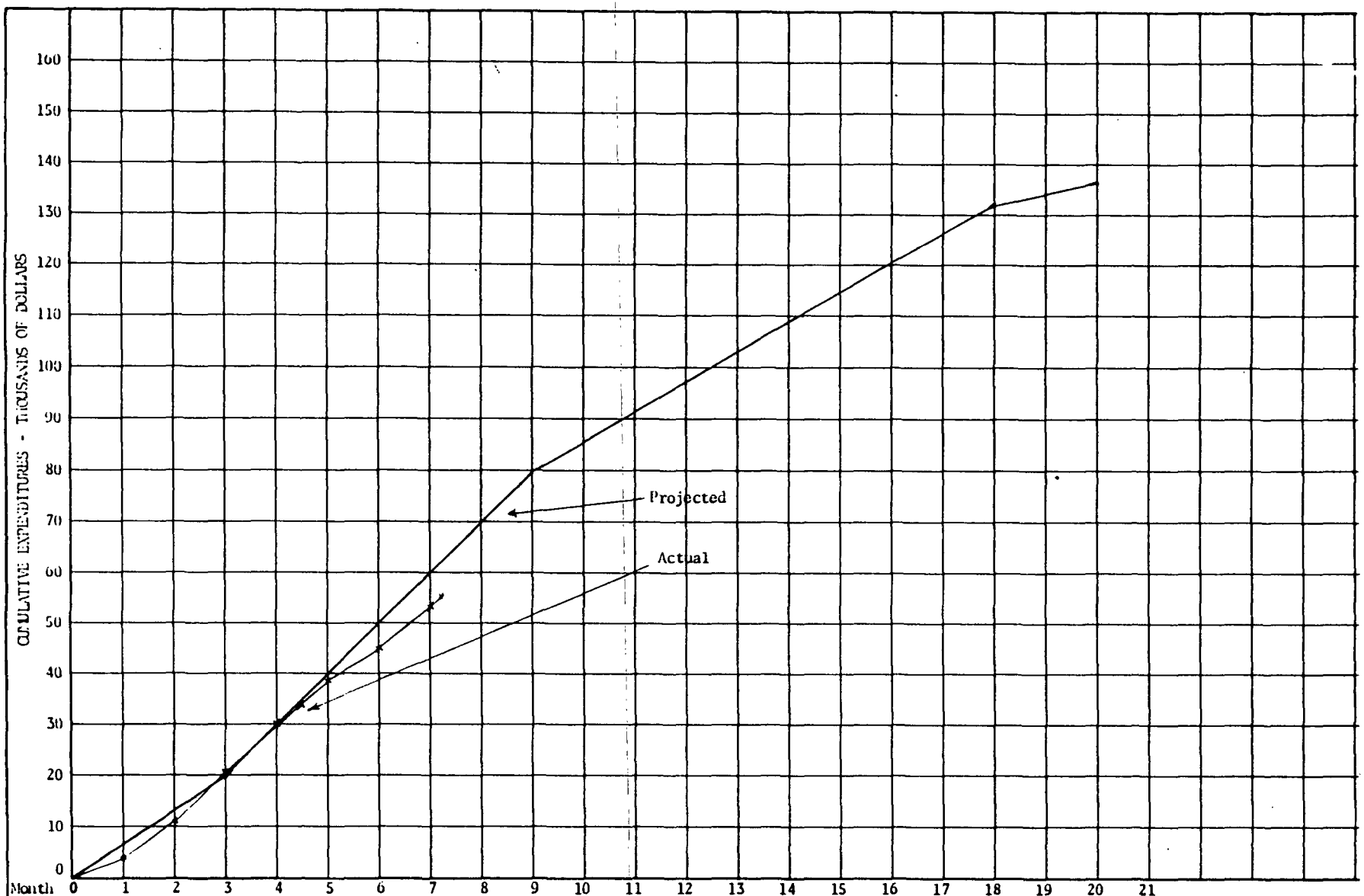

SUBJECT ANTICIPATED EXPENDITURE VS TIME CURVE, INVESTIGATION OF SMELT-WATER REACTIONS FOR FOURDRINIER KRAFT INSTITUTE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
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TRIMONTHLY PROGRESS REPORT
COVERING WORK FROM AUG. 15 TO NOV. 6, 1964

To

Dr. H. S. Gardner, Project Coordinator
The Institute of Paper Chemistry

Submitted by
Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

NO. 3 PROGRESS REPORT ON THE COMBUSTION ENGINEERING PROGRAM FOR DETERMINING THE NATURE OF AND REMEDIES FOR EXPLOSIVE REACTION(S) BETWEEN SMELT AND WATER IN KRAFT CHEMICAL RECOVERY FURNACES

Explosion Mechanisms

The previous report contained a theoretical model (Fig. 2) of encapsulation with a low smelt-to-water ratio. This geometry would most likely occur if smelt were introduced into a relatively large pool of water in the furnace or in a dissolving tank. Current studies have shown that explosions also result when a small proportion of water is forced below the surface of molten smelt. Figure 1 is an idealized model of the system with a high smelt-to-water ratio used in current experiments. Here a single shell of frozen smelt, rather than the double shell produced by smelt immersed in water, serves for encapsulation.

At this point it may be well to review some fundamentals of an explosion process[1]. An explosion may be defined as a sudden release of pressure regardless of the source. Explosions can be produced by various physical or chemical phenomena. The explosion of a steam boiler is produced by the rapid release of steam and the change of heated liquid water into a vapor. The explosion of a heated cylinder containing compressed air is caused by an increase in pressure. The process in both cases is called an explosion, but neither substance is an explosive in the commonly accepted use of the term. In both cases the explosion arises as a result of overcoming resistance of the container walls, and its destructive effect depends on the pressure of the steam or gas in the container. The work accomplished during an explosion is due to the rapid expansion of gases or vapors independently of whether they already exist or are formed at the time of the explosion.

The rate of energy release as well as its amount is critically important in determining the extent of damage. Small explosion hazard is produced by a boiler tube rupture but the same quantity of energy released over a shorter period of time, due to a boiler drum rupture, can create real damage due to the shock wave produced. It is the high rate of energy evolution from chemical type explosives which defines their advantage over ordinary fuels. (The total quantity of energy per unit weight of an explosive is much less than that of a normal fuel.)

A comparison of chemical gaseous hydrogen-oxygen explosions with a physical condensed phase water encapsulation explosions generates some interesting differences. The explosion of gaseous systems (as contrasted with solid or liquid) does not usually

result in an increased volume of reaction products. In some cases the explosive transformation is even accompanied by a decrease in volume.

For example the explosion of a stoichiometric mixture of two volumes of hydrogen and one of oxygen results in a decrease of one-third in volume since three mols of reactant gases give two of product, water vapor.

$$2H_2 + O_2 \longrightarrow 2H_2O + 2{:}57.8 \text{ Kcal}$$

However, this decrease in volume is more than compensated for by the exothermic nature of the reaction which causes rapid thermal expansion of the water vapor formed. The pressure produced, about 147 psi. (10 atmospheres), is quite low compared to that from commercial liquid and solid phase explosives which attain hundreds of thousands of atmospheres in hundred-thousandeths to millionths of a second. It is nevertheless far above the level that chemical recovery furnaces are built to withstand.

The large volume of a unit weight (specific volume) of gaseous exploding systems like hydrogen-oxygen, dictates that the energy released per unit volume of exploding material (energy density) will be quite low. This means that the pressure on a unit area of the relatively large surface surrounding the exploding gases is also comparatively low. Liquid water, a condensed phase material, occupies a 2035 times smaller volume per unit weight than the hydrogen-oxygen mixture (at 25°C) which forms it. Therefore the energy density from a physical explosion of encapsulated water could theoretically be much higher than that of a combustible gas explosion if the tensile strength of the encapsulating shell were high enough.

This brings up the question of how a shell of frozen smelt could achieve the strength required for explosive damage. The high heat transfer rates required are more readily understandable due to direct contact between smelt and water. A possible explanation was provided by Dr. A. R. C. Westwood[2] who discussed the significant enhancing influence of corrosive liquid environments on the strength and ductility of solids, i.e., the Joffe effect. For instance, a salt crystal is weak and brittle if deformed in air, but up to 25 times stronger and considerably more ductile if it is deformed in water. High strength in a smelt shell may result from its contact with two corrosive liquids, molten smelt on the outside, and water on the inside which would tend to eliminate sources of strength-impairing coatings and surface dislocations (notches, cracks, etc.). The rapid crystallization of smelt due to direct water contact might also tend to produce fine-sized stronger grain structure. We have so far not been able to recover any recognizable fragments of an encapsulating shell on which to make strength measurements.

Dr. H. S. Gardner pointed out recently that the maximum theoretical pressure produced from encapsulating a tablespoonful of water by molten smelt may be as much as ten times higher than the 72,800 psi calculated (Progress Report No. 2) assuming that water behaved as an ideal gas. Its deviation from ideal behavior makes this sizable correction apropos. Either calculation of course assumes a shell strong enough to contain the water, which we know from experimental evidence is never the case. A water addition either evaporated on smelt surface or caused an explosion. Enormous shell strength would be required to contain water at temperatures near 1500°F. The fact that the shell does allow temporary containment of liquid water and considerable pressure build-up in the capsule, however, may well account for the sudden release of a burst of energy and damage created by resulting shock waves when this shell ruptures.

Apparatus and Test Method

Mr. Charles L. Norton has aided and advised on all test work in this and the earlier reports. He has also been responsible for gas chromatographic analyses. All tests described in the current report involved quenching 400 g. quantities of molten kraft smelt made from pure sodium carbonate and fused sodium sulfide. About 30-35% Na_2S (by analysis) was used since this composition consistently gave violent explosions when small quantities of water were injected beneath the surface of molten smelt in the proper temperature range. The same general procedure for mixing water and smelt has been employed in current work, i.e. the successive forcible injection of a series of equal volumes (3 ml.) of room temperature water below the smelt surface until one produces an explosion. Once the critical smelt temperature range has been reached, almost every injection subsequent to the first explosion produces another explosion until a smelt temperature of about 1500°F. is reached. The particular injection of a series which will explode can often be predicted since its immediate predecessor usually "spits", i.e., audibly ejects a small quantity of smelt from the crucible. This phenomenon probably indicates that the appropriate smelt temperature for heat transfer at an explosion-creating rate is close at hand.

Further injections after the first major explosion occurs are no longer made since subsequent explosions with the small amounts of smelt left are quite destructive to the graphite crucible even though of reduced intensity.

Experimental

A. Introduction

The basic reason for C.E.'s emphasis on explosive experiments is the belief that "one experiment is worth a thousand expert opinions." First hand knowledge gained by close observation of explosions safely as they occur and by studying the complex interaction of variables which govern them is indispensable for reaching the ultimate goal rapidly, a practical preventive measure for smelt-water explosions in chemical recovery furnaces.

In order to speed this practical solution, experiments on remedial measures are being started even though knowledge of mechanism is not complete. Study so far has suggested several categories of materials which might be added safely to molten smelt on a furnace bottom for cooling it quickly below explosion temperature, approx. 1500°F. A search is being made for water solutions (which have high heat capacity) of materials which can even be injected beneath smelt (the extreme case) without causing an explosion. Water solutions might also produce large volumes of furnace inerting steam (if the water-gas reaction with char were not significant.)

B. High Vapor Pressure Additives for Water

It was reasoned that ammonium bicarbonate solution is thermally unstable and decomposes on contact with molten smelt into gases which either (a) promote almost instantaneous vapor blanketing of encapsulated water, or (b) produce foam which results in the encapsulation of a relatively small proportion of liquid water-to-gas, or (c) prevent encapsulation due to production of large volumes of gases. Using this same line of reasoning we also tried small proportions of high vapor pressure liquids in the quench water.

In runs Nos. 59 and 60, no violence was produced by a continued succession of 3 ml. injections of 10% (by vol.) methyl alcohol into molten smelt until it solidified. The smelt in blank run No. 58 exploded violently after only three injections of water since its initial temperature, 1565°F., was already in the critical range. With alcohol, flames rose 6" high above the crucible following each injection, because of its flammable nature. Run No. 61 showed that 5% methanol solutions were almost too dilute to be effective. Presence of only 0.01% Minnesota Mining & Manufacturing fluorocarbon surface active agent L1159 in the 5% methanol, however, seemed to restore its beneficial action.

Runs No. 63-67 showed similar behavior for ammonium bicarbonate solutions. These with surfactant would seem the best candidate for furnace use since the decomposition products, NH_3, H_2O, and CO_2 would be non-flammable in this equimolar proportion.

The surfactant would aid in penetrating black ash in the bed. None of the decomposition products of the ammonium salt would be expected harmful to pulping since their existence in the recovery cycle would be fleeting in this alkaline medium. However, these experiments are not conclusive and much more work remains to be done before a recommendation could be made.

Ammonium hydroxide, also a producer of gaseous ammonia on heating, was effective down to 5%. Isopropanol, an alcohol of higher molecular weight, performed in like manner.

C. Tube-Leak Simulated Water Addition

Runs 73-79 were made in a manner to simulate a small tube leak which squirts water continuously on a limited area of molten smelt surface, but without enough velocity to force water beneath the surface. Vigorous boiling in run No. 73 took place for 20 seconds as water was added at 100 ml/15 sec. from a one liter reservoir with 1/8" id. outlet tube placed 3" above smelt surface. A 2" depth of solution had accumulated on top of the smelt at this time. A loud explosion then resulted which blew most of the smelt out of the crucible. A second but lesser explosion followed about ten seconds later. Starting smelt temperature was 1820°F.

A similar experiment, Run No. 74, was made at about five times slower water addition rate. A continuous crackle but no explosion took place. The next run, No. 75, was with cooler smelt (1650°F.) at the higher water addition rate. Mild pops but no violence took place with addition of a liter of water in this manner. No. 76, with water addition at the higher rate and high smelt temperatures, checked results from No. 73. A series of 5-7 explosions of mounting intensity took place after a short induction period.

This is the same behavior which recovery boiler operators describe for a water wall tube leak into molten smelt in the furnace. Evidently both initial smelt temperature and water addition rate are important for determining the occurrence and violence of smelt-water interaction. A comparison of injected water with continuously added water experiments suggests that the turbulent interface between molten smelt and a body of water floating on it causes water to become entrapped beneath the smelt. This is a significant discovery and means that water does not have to be added with substantial penetrating velocity in a furnace to cause an explosion.

Run 77 added 10% NH_4HCO_3 solution continuously to molten smelt surface. No violence was produced and the smelt became solidified and dry on its upper surface after 5 minutes. In a cleanup operation more solution was added to dislodge the thermocouple frozen in the surface and an unexpected muffled

explosion resulted. This explosion dislodged ½" thick chunks of solid smelt. (All other explosions have blown out liquid smelt.) The crater revealed a core of molten smelt surrounded on all sides in the crucible by solidified smelt. Perhaps there is a parallel here with the long-delayed explosions in a water-flooded furnace. Solidified smelt has a low thermal conductivity in the same category as Pyrex glass or chalk. Thus the insulation provided by a solid crust of frozen smelt and/or black ash on the surface might preserve a core of smelt in the molten condition for prolonged periods. Cooling fissures might later provide the contact necessary for a delayed smelt-water explosion.

Neither No. 78 with 0.01% L1159 surfactant in the 10% NH_4HCO_3 solution added at 100 ml/17 sec., nor No. 79 at a slower addition rate, produced any violence when added continuously in the same manner. These results confirmed earlier injection findings that a surface active agent can enhance inhibition of smelt-water explosions.

A wide variety of surfactant solutions by themselves with no gas-producing chemical have not prevented explosions when injected at room temperature. Future experiments will be tried using them as hot solutions in order to combine wetting action with the higher vapor pressure of hot water.

D. Effect of Smelt-Weakening Additives

Considerable thought has been given to the possibility of continuous addition of a small proportion of material to the black liquor or smelt which would decrease the tensile strength of smelt so that the frozen shell of smelt generated by encapsulation would be too weak to allow buildup of dangerous pressures before rupture. This material would render kraft smelt, like sodium carbonate, non-explosive or of greatly reduced explosion capability. The requirements for such a material are exacting. It should be: effective in small proportion, cheap, and non-contaminating in the recovery and pulping cycles. The following materials have been tried in 5% concentration in smelt without success: MgO, C, CaO, SiO_2, Al_2O_3, SiC, Fe_3O_4, $MgSO_4$, K_2CO_3, Li_2CO_3, and green liquor dregs. First effort has centered on finding any materials which inhibit explosions. Candidates could be selected later which would not interfere with pulping or which could be easily eliminated from the recovery system, say in the green liquor dregs.

Smelt additives seem fundamentally more promising than quenching solutions since they would not permit the smelt to explode. Smelt weakeners would hence not require quick-acting application devices to operate when a tube leak occurs as would be necessary for smelt quenching solutions.

E. Smelt Introduction into Strong Black Liquor

A final run, No. 80, was made to assess the behavior of strong black liquor trapped under molten smelt. A 400 g. batch of molten 1823°F. smelt was poured slowly into about an equal volume (3" depth) of 160°F. strong (50% solids) kraft black liquor. Vigorous boiling was effected and after 10 minutes the entire liquor charge was pyrolyzed into friable char-like black ash. No violence was noted and only 0.2% hydrogen was found in the exit gases. The results correlate with those of Progress Report No. 2 in which injections of strong black liquor on molten smelt surface did not cause violence either. Possibly the pyrolysis of black liquor organics absorbs heat rapidly and causes smelt and liquor to become separated by an insulating char layer. In any event, the possibility of an encapsulation type explosion with only strong black liquor and smelt seems remote in laboratory experiments to date.

F. Encapsulation Explosions versus Combustible Explosions

Table II shows results from a number of experiments in which the composition of smelt blown from the crucible on water addition and the gases before explosion were compared. Results indicate that a small proportion of sodium sulfide is oxidized to sodium sulfate (if oxidation of the solid by air contact in the 2 minute period before sampling can be ignored) in the explosion process. There was no evident correlation, however, between proportion of hydrogen found in the cumulative gas samples and the magnitude of explosive violence observed. The proportion of hydrogen did seem to correlate roughly with the amount of sulfate created.

Further data are shown in Table III on change of sodium sulfide content of smelt by explosion, again discounting air oxidation of cool, solid Na_2S since samples were taken quickly following an explosion. Minor changes in Na_2S content were shown in most cases. Each gas sample was taken at one smelt temperature after a single water addition rather than being accumulated in small increments over a range of temperatures as before. Here also hydrogen values were low, in every case well below the explosive limit in air. Careful checking of the "firecracker-like" odor from smelt quenches has proven that it is produced by water contact with smelt whether explosions occur or not. Even quenches of molten sodium carbonate give traces of the same smell. It disappears after about one-half hour standing in gas pipets, either dry or wet. Sodium compound dusts seem the most likely source.

Even if the Na_2S-H_2O reaction to yield H_2 and Na_2SO_4 were highly efficient and self sustaining under these conditions instead of endothermic, the dilution of sodium sulfide with 70% of inert sodium carbonate in smelt would be expected to severely limit the reaction rate. These results may mean that sodium sulfide and water do react to form hydrogen at high smelt

temperatures but that the combustion of hydrogen produced is a side reaction not responsible for the explosion damage observed in these laboratory experiments.

G. Pressure Wave Measurements

A limited number of experiments have been conducted in measuring the pressure of the shock wave produced by these scaled-down laboratory experiments which use only 3 ml. of water. The pressure registered on some of the most violent ones ran 80-90 psi. 4 5/8 inches away from the explosion site. By applying the approximate inverse square law this would amount to about 5400 psi or 367 atmospheres one radius away from the exploding capsule itself, assuming a 3 ml. sphere. This pressure is 36 times the explosion pressure generated by hydrogen-oxygen mixtures. Care should be used in applying these values since we cannot be sure that flying smelt particles did not strike the orificed transducer diaphragm. These measurements will be refined and checked in future work. The probe has been calibrated suitably but additional experience must be accumulated in determining the proper direction and distance for mounting it. Blasting caps (T1 BP #2) have been used to get a better evaluation of directional effects, but they produce shrapnel which may damage the transducer diaphragm. A 22 caliber blank pistol has been bought for this purpose. A high speed chart drive for the Visicorder has been ordered to get a better idea of the shock wave pressure decay with time. The current slow drive speed allows only a measurement of pressure intensity.

Spherical Explosion Chamber

The spherical explosion chamber has now been completed and mounted in Kreisinger Development Lab. (See Figure 2). Mounting over an existing pit avoided the need for expensive supersturcture. The pneumatic cylinder for loading and positioning the smelt crucible has arrived and will be mounted in the pit. A high pressure sight glass will cover the open flange to the left. Other parts of the test set up are being assembled and tested as they come. The induction heating furnace has been installed and is used continuously for melting smelts for experiments in the plywood barrier. It is a reliable instrument which has greatly speeded work on the project.

Future Work

A promising method for determining tensile strengths of smelt has been found in a recent reference(3). It employs

the crushing strength of a horizontal cylinder to calculate tensile strength of ceramic materials.

A computer calculation of heat transfer rates between encapsulated water and molten smelt has been scheduled. This will allow us to make reasonable approximations of the pressure inside the capsule, since the time to rupture is known. Such pressures could then be related to shell strength and the intensity of shock waves measured by the pressure transducer for a more complete assessment of forces produced by smelt-water explosions.

Ektachrome pictures of explosions taken at 32 frames per second were too slow to show important details. High speed movies of the encapsulation explosion process will be made in the plywood booth at 100 to 8000 frames per second. These may lead to a better understanding of the mechanics of an explosion. They will also allow familiarization with high speed photographic equipment prior to its use on the spherical explosion chamber.

The effects of aqueous solutions on hot char will be studied to make sure that their interaction itself does not create explosive gases. If chemicals dissolved in water continue to prove effective in preventing explosions, their decomposition products will likewise be investigated for flammability.

Wharton Nelson

WHARTON NELSON
Senior Project Engineer
November 11, 1964

REFERENCES

1) Material in this section has been taken liberally from an excellent Russian treatise, "Physics of an Explosion" by F. A. Baum, K. P. Stanynkovich, and B. I. Shekhter, AD 400151, T1488 a-q, Defense Documentation Center for Scientific and Technical Information, Cameron Station, Alexandria, Virginia. (1959) Unclassified, U. S. Army Engineer Research and Development Laboratories, 954 pages, ASTIA.

2) Westwood, A.R.C. "Surface Sensitive Mechanical Properties", Industrial and Engineering Chemistry, Sept. 1964, Vol. 56, No. 9, pp. 14-25.

3) Spriggs, R. M., Brissette, L. A., and Vasilos, T., "Tensile Strengths of Dense Polycrystalline Ceramics by the Diametral-Compression Test", Materials Research and Standards, May 1964, pp. 218-220.

TABLE 1

Further Quenching Experiments

Run No.	Quench Liquid	Results	Init. Smelt Temp.	Smelt Temp. for Explosions	% H_2
58	Blank - 3 ml. water	Violent expl. on 3rd injection	1565	1508	0.14
59	3 ml. of 10% methanol in water	No violence after 11 injections	1760	None	-
60	Repeat of No. 59	No violence after 14 injections	1760	None	1.74
61	3 ml. of 5% methanol in water	Mild pops on No. 13 - 17	-	None	-
62	3 ml. of 5% methanol in 0.01% L1159	No violence after 23 injections	1820	None	-
63	4 ml. of 10% NH_4HCO_3 in water	No violence after 17 injections	1618	None	0.45
64	4 ml. of 5% NH_4HCO_3 in water	Mild bang after 15 injections	1740	1372	0.84
65	3 ml. of 5% NH_4HCO_3 in 0.01% L1159	No expl. after 20 injections	1800	None	-
66	Repeat of No. 65	No expl. after 27 injections	-	None	-
67	3 ml. of 2% NH_4HCO_3 in 0.01% L1159	Mod. expl. on No. 9	1820	1630	-
68	3 ml. of 10% NH_4OH in water	No violence after 25 injections	-	None	-
69	3 ml. of 5% NH_4OH	No expl. after 20 injections	1735	None	-
70	3 ml. of 2% NH_4OH	Violent* expl. on No. 11	1825	1565	-
71	3 ml. of 10% isoproponol in 0.01% L75	No violence after 14 injections	1795	None	0.98
72	3 ml. of 5% isoproponol	20 injs. produced only pops	1840	None	-
73	Water-contin. stream, 100 ml/15 sec.	Loud expl. in 20 sec; 2nd lesser expl.	1820	-	-
74	Water-contin. stream, 100 ml/72 sec.	After 60 sec., contin. crackle	1820	None	-
75	Water-contin. stream, 100 ml/17 sec.	Series of mild pops after 10 sec.	1650	None	-
76	Water-contin. stream, 100 ml/17 sec.	Series of expl. incr. in violence	1950	-	-
77	10% NH_4HCO_3 contin. stream, 100ml/17sec.	Delayed, mod. expl.	1850	-	-
78	10% NH_4HCO_3 in 0.01% L1159 contin.addn.	No expl. or violence	1825	None	-
79	Same except 100 ml/32 sec.	No expl. or violence	1825	None	-
80	50% black liquor-400 g smelt poured in	No expl. or violence	1823	None	0.2

Note* Explosion broke cruicible.

TABLE II

CHANGE IN SODIUM SULFATE CONTENT DUE TO EXPLOSIONS

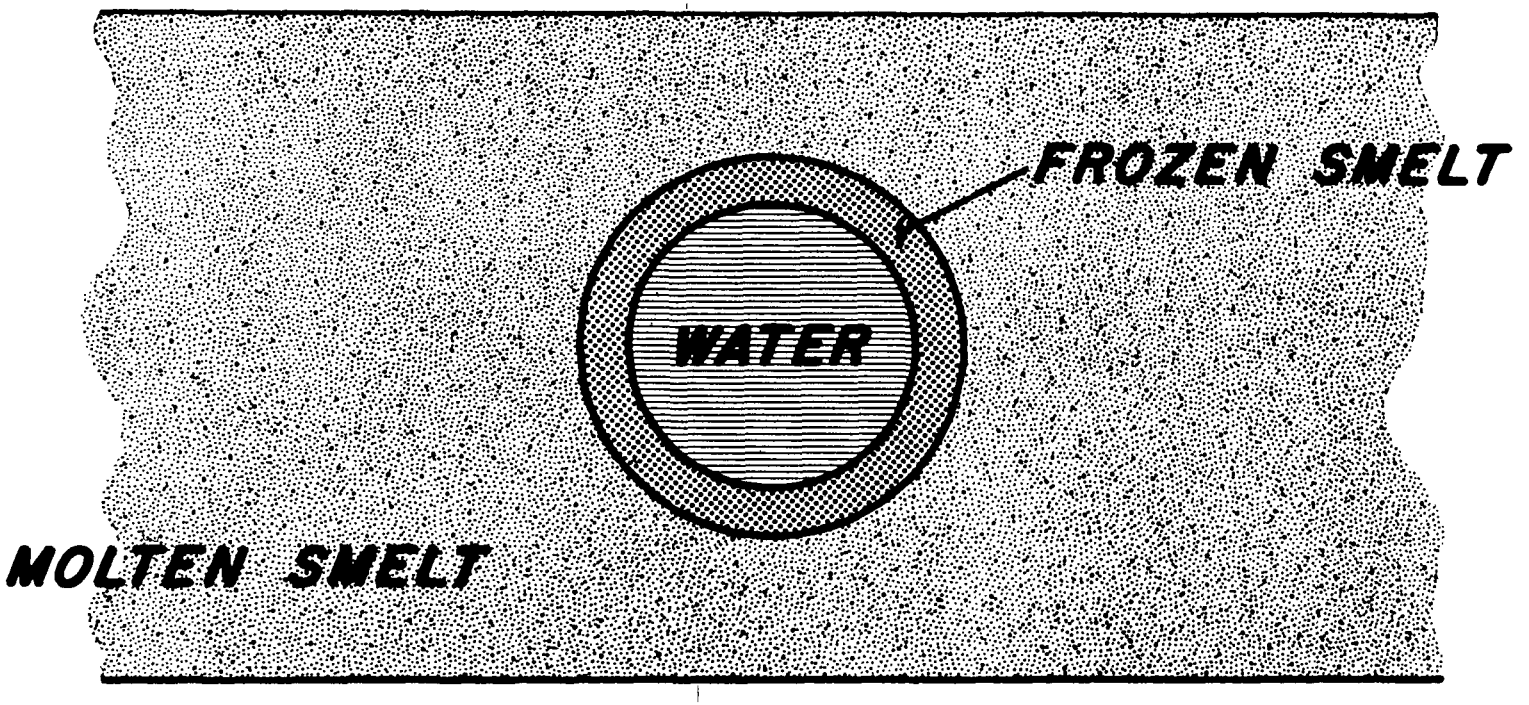
Run #	% H_2	Results	% Na_2SO_4 Before	% Na_2SO_4 After	% Na_2SO_4 Increase	Conditions
54	0.36	Small Pops	5.98	6.45	0.47	2 ml. water - Gently Added
40	0.51	2 Mild Pops	1.36	4.65	3.29	2 ml. 15% Na_2CO_3 solution
42	0.42	Mild Pops	2.01	2.75	0.74	2 ml. 15% NaCl solution
-	0.06	Violent Expl.	1.97	1.98	0.01	2 ml. water
52	0.06	2 Mild Bangs	3.69	3.95	0.26	4 ml. 35% Black Liquor

TABLE III

CHANGE IN SODIUM SULFIDE CONTENT OF SMELT BY EXPLOSION

RUN	BEFORE EXPLOSION	AFTER EXPLOSION FROM ROOF	AFTER EXPLOSION IN CRUCIBLE	EXPLOSION	% H_2	Smelt Temp. Taken
A	31.3	30.5	31.3	Violent	-	-
B	30.2	31.0	30.5	Muffled	-	-
C	24.8	23.1	20.8	Moderate	-	-
D	21.9	-	21.4	None	0.62 0.33 0.36	1830° 1760° 1610°
E	35.3	33.5	-	Very Violent	0.31 1.10	1790° 1730°
F	27.8	27.4	-	Very Violent	1.3 2.2 1.5	1820° 1760° 1690°

(high smelt-to-water ratio)



Physical Encapsulation Explosion Model

FIG. 1

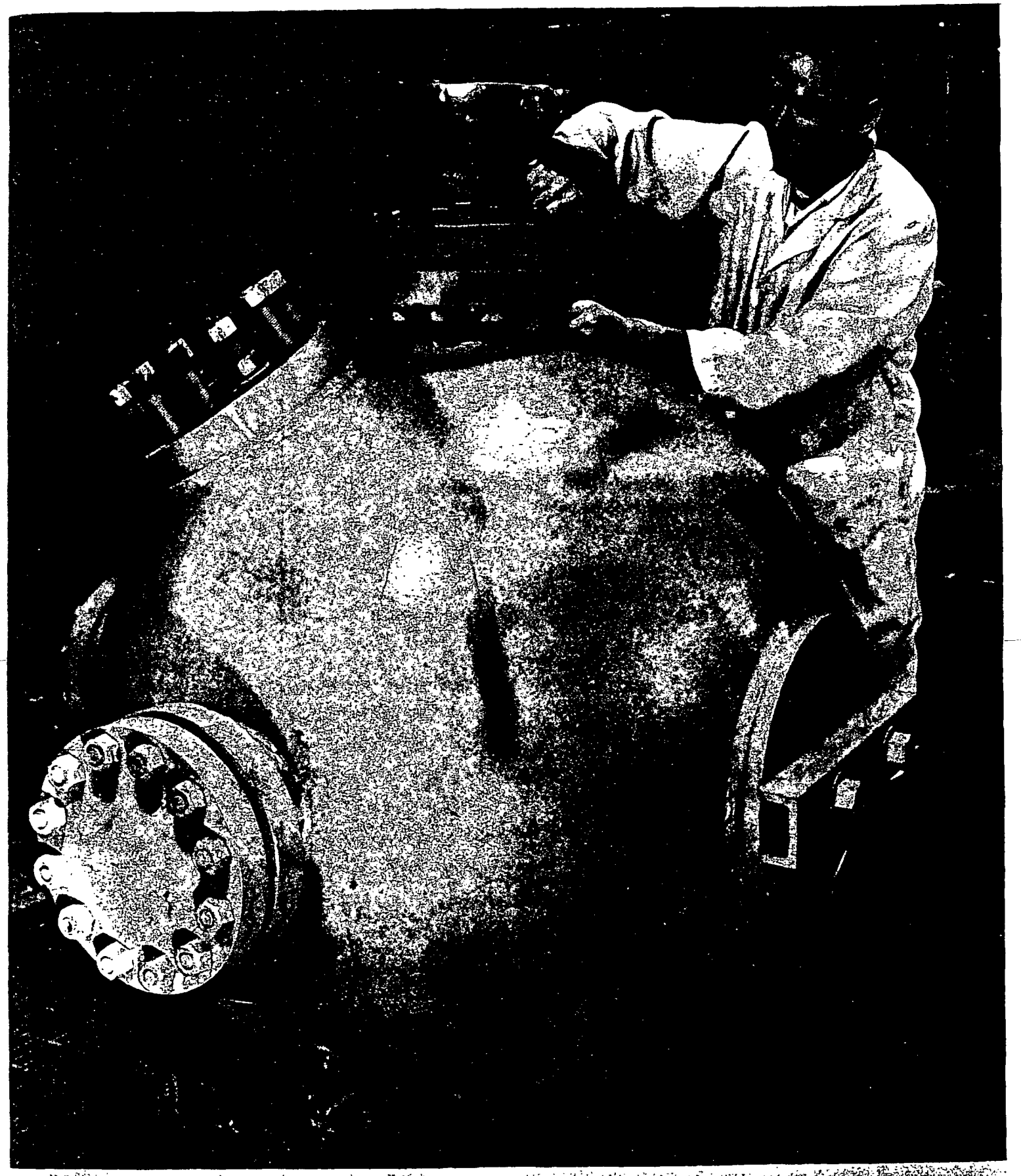


FIGURE 2